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A novel approach for description of non-covalent intermolecular interactions

Dissertation Thesis Abstract

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Introduction

Non-covalent interactions play a major role in many important physical, chemical, and biological processes that include, for instance, inter-molecular interactions between biomolecules, adsorption and separation, self-assembly in supra-molecular chemistry, and catalytic activity. To gain a deeper understanding of such processes at the atomistic level it is often necessary to investigate these systems theoretically. Due to the complex character of relevant systems, realistic models include hundreds of atoms and, thus, the computational investigation must rely on rather approximate methods. An accurate description of these systems still represents a major challenge for theoretical chemists.

Methods based on density functionals (density functional theory, DFT) are currently among the most popular approaches for computational treatment of large systems. Unfortunately, the non-covalent interactions cannot be reliably calculated within the DFT framework due to the fact that DFT does not account for the description of dispersion interactions. Many attempts have been made to overcome this deficiency of DFT in the past decade; computationally affordable and reliable solution has not been found yet. The development of such methodology (affordable and reliable) was the main subject of this thesis. A four year effort has resulted in formulation of the DFT/CC method (density functional theory corrected for coupled clusters accuracy).

The performance of the DFT/CC method has already been demonstrated for various systems, including weakly bound molecular clusters, molecular crystals, and adsorption processes of small molecules on graphene/graphite and in microporous materials. Results obtained with the DFT/CC method for these systems are currently among the most reliable theoretical estimates and, for large systems (e.g., graphitic materials and microporous materials) they are the only reliable estimates available.

Methods

Significant effort has been exerted to overcome the DFT error in accounting for dispersion interaction. The development of truly non-local density functional would be most desirable. However, the functional form is still eluding, even though some promising attempts has been made. The use of the symmetry adapted perturbation theory (SAPT-DFT) has also shown extended accuracy. This method is, however, rather expensive and less appropriate for large scale applications. Empirically corrected DFT approaches (often denoted as DFT-D where D stays for dispersion) are currently implemented in many quantum chemical codes. The pair-wise atom-atom approximation is assumed along with the R^{-6} asymptotic dependence of the dispersion correction to DFT. Moreover, an exponential damping function is applied in the repulsion region of the intermolecular potential function. The novel DFT/CC method formally belongs to the class of empirically corrected approaches. In the DFT/CC approach,

however, no a priori functional form of the pair-wise atom-atom correction functions is assumed. Larger complexity of the DFT/CC method is fully compensated by very high accuracy of obtained results compared to the simple DFT-D approaches. The energy difference between the reference level of theory (typically CCSD(T) at the complete basis set limit) and DFT is calculated for an appropriate set of molecules

$$\Delta E = E_{\mathrm{CCSD(T)}} - E_{\mathrm{DFT}} \tag{1}$$

The essential assumption of DFT/CC is the pair-wise representability of the DFT error, ΔE, which can be described by the following equation

$$\Delta E = \sum_{i}^{N_a} \sum_{j}^{N_b} \varepsilon_{ij}(R_{ij}), \tag{2}$$

where N_a and N_b are numbers of corresponding atoms of each monomer and R_{ij} is the interatomic distance between atoms i and j. The transformation of ΔE into atom-atom correction functions $\varepsilon_{ij}(R_{ij})$ is performed through the Reciprocal Power Reproducing Kernel Hilbert Space interpolation (RP-RKHS) with R^{-6} and R^{-8} asymptotic behavior by means of singular value decomposition (SVD) algorithm. Apart from the pair-wise approximation additional assumptions are made: *(i)* the anisotropy of the atom-atom correction function is neglected, *i.e.* correction function dependence on monomer orientations is negligible, and *(ii)* the inter-system transferability of the correction functions is preserved. The second assumption is crucial and needs to be carefully tested for each studied system by comparing DFT/CC results against CCSD(T)/CBS calculations on an additional set of molecules as close to the system of interest as possible.

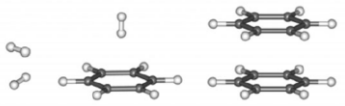

Fig.1 Definition of the reference set: hydrogen dimer (D_{2d}), hydrogen-benzene complex (C_{6v}) and benzene dimer (D_{6h}) were used for the evaluation of H-H, C-H and C-C correction, respectively.

Results

Non-covalent molecular complexes

The benzene dimer is the most commonly used benchmark system for testing computational approaches in connection with non-covalent interactions. The reference set for evaluation of the DFT/CC corrections is depicted in Fig. 1. The tilted T-shape like structure having the C_s symmetry was found to be the global minimum on the benzene dimer potential energy surface (PES) - about 0.4 kJ/mol more stable than the parallel displaced (PD) structure

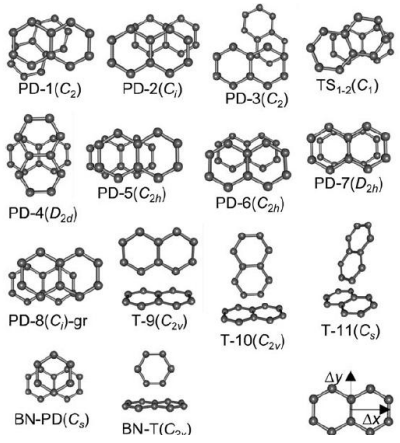

Fig.2 Localized stationary structures of naphthalene dimer and benzene-naphtalene complexes (BN). The complexes are classified as either parallel displaced (PD) or T-shaped (T). Symmetry is given parentheses.

corresponding to the most stable stacking arrangement. The results are consistent with CCSD(T)/CBS calculations and can be used as benchmarks for similar type of calculations.

Subsequently, the PES's of benzene-naphthalene and naphthalene dimer were investigated. The stationary structures are depicted in Fig.2. The results of the DFT/CC method are fully consistent with the best available data in the literature and the estimated error does not exceed 0.8 kJ/mol. The global minimum T-shaped structure has been found only for the benzene dimer. Larger aromatic molecules strongly prefer the parallel displaced stacking arrangement.

Molecular crystals

The extension of DFT/CC for solid state calculations with imposed periodic boundary conditions is straightforward. The modeling of solid state properties requires very accurate and transferable correction functions due to many intermolecular interactions involved. Moreover, the zero point vibrational energy (ZVPE) correction has to be taken into account. The solid benzene, naphthalene, anthracene, graphite, and solid C_{60} were investigated. In these solids the dispersion interactions are dominant and consequently the uncorrected DFT calculations provide only a small fraction of the total cohesive energy of the crystal. This kind of behavior is demonstrated on cohesive energies and inter-plane equilibrium distances of graphite (see Table 1). In contrast, the DFT/CC structural parameters and cohesive energies resemble closely the experimental observations. Similar accuracy has been obtained for the rest of molecular crystals. The cohesive energies are accurate to within 10 meV/molecule and the equilibrium distances are within hundredths of angstrom from the corresponding experimental values.

Table 1 The equilibrium lattice constants (*a,c)* and cohesive energies of graphite

Methods	a/Å	c/Å	E_{coh}/[meV/atom]
DFT(PBE)	2.461	~9.0	~3
DFT(vdW-DF)	2.470	7.52	24
DFT-D			66
DFT/CC	2.463	6.55	57
DFT/CC + ZPVE	2.463	6.60	54
Experiment	2.460	6.67	52 ± 5

Adsorption of small molecules on graphene/graphite

The adsorption on carbon based materials has its industrial importance. The materials can be utilized as a storage medium for molecular hydrogen or nowadays carbon dioxide. The graphene/graphite presents an ideal starting point for modeling of such adsorption processes on carbon based materials. The advantage of graphene/graphite system stems from the fact that it is well characterized structure and experimental adsorption enthalpies of many molecules are known. It is straightforward that graphene sheet mimics the graphite system more

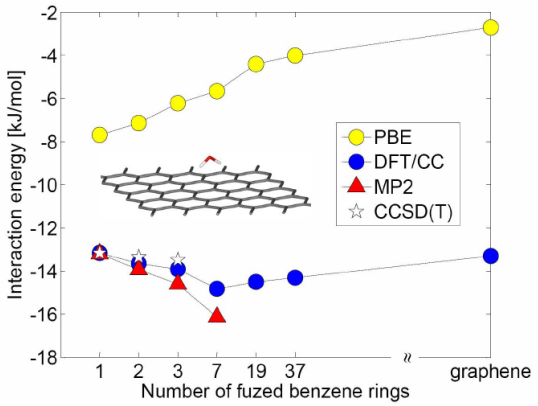

Fig. 4 The interaction energies of water-PAH and water-graphene complex (circumflex structure) depending on number of fused benzene rings for DFT(PBE), DFT/CC, MP2 and CCSD(T) methods.

closely than PAH molecules, where the convergence with respect of its size needs to be established (see Figure 4). Twelve different graphene..A complexes, where A stand for Ar, H_2, N_2, CH_4, C_2H_6, C_2H_4, C_6H_6, C_2H_2, CO, CO_2, H_2O and NH_3, were investigated. The comparison with experimentally determined adsorption enthalpies is rather exceptional. In case of H_2 the full vibrational dynamics on the graphene surface was conducted. The agreement with experimentally determined spectra is very good, but not fully quantitative (error of 15 cm^{-1}).

Adsorption of CO_2 and H_2 at porous materials

The alkali-metal exchanged zeolites are of particular interest as CO_2 adsorbents. The interaction strength can be tuned by changing the metal cation, cation concentration and topology of the zeolite. The isosteric heats of adsorption for CO_2 in ferrierite were calculated by means of the DFT/CC method in an excellent agreement with experimentally determined values. The most stable adsorption sites are formed on a pair of extra-framework alkali-metals cations (dual cation sites). Adsorption complexes on dual cation sites were found to be about 10 kJ/mol more stable than those formed on isolated cation sites (see Fig.5). Similar study was conducted for H_2 adsorption at Ca^{2+}-LTA. Two different adsorption sites were located with substantial different adsorption enthalpies (8.3 kJ/mol and 19.5 kJ/mol). Both sites also exhibit very different frequency shifts of H-H vibration (-84 cm^{-1} and -351 cm^{-1}). The VTIR measurements strongly support the presence of just one adsorption site (frequency shift of 80 cm^{-1}). The more stable adsorption site is either not present or is invisible in IR measurements due to symmetry considerations.

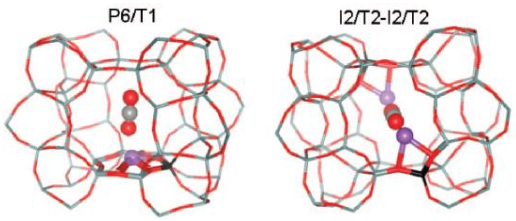

Fig. 5 Adsorption of CO_2 at K^+-FER with definitions of single (left) and dual (right) cation sites. Topology of each site is also given.